

FORM PCT 1390
REV. 5/93

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NO
BENJE-1 (PCT)TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U S APPLICATION NO (if known, see 37 CFR 1.5)

09/936335

INTERNATIONAL APPLICATION NO.
PCT/EP99/07649INTERNATIONAL FILING DATE
OCTOBER 12, 1999PRIORITY DATE CLAIMED
MARCH 12, 1999

TITLE OF INVENTION

METHOD OF PRODUCING ETHYLENE (DI)CHLORIDE (EDC)

APPLICANT(S) FOR DO/EO/US
MICHAEL BENJE

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371 (f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau)
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has **NOT** expired.
 - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

PCT/ISA/210 - Int'l. Search Report
3 Sheets of Formal DrawingsApplicant Claims Priority under 35 U.S.C. §119 of German Application No. 199 10 964.8 filed March 12, 1999.
Applicant Claims Priority under 35 U.S.C. §120 of: PCT No. PCT/EP99/07649 filed October 12, 1999.

APPLICATION NO. (if known, see 37 CFR 1.5)

09/936335INTERNATIONAL APPLICATION NO
PCT/EP99/07649ATTORNEY'S DOCKET NO
BENJE-1 (PCT)☒ The following fees are submitted:**Basic National Fee (37 CFR 1.492(a)(1)-(5)):**

Search Report has been prepared by the EPO or JPO\$860.00

International preliminary examination fee paid to USPTO (37 CFR 1.482)

.....\$690.00

Neither international preliminary examination fee paid (37 CFR 1.82) nor
international search fee (37 CFR 1.445(a)(2)) paid to USPTO\$1,000.00International preliminary examination fee paid to USPTO (37 CFR 1.482)
and all claims satisfied provisions of PCT Article 33(2)-(4).....\$100**ENTER APPROPRIATE BASIC FEE AMOUNT =**

\$ 860.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ____ 20 ____ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

Claims	Number Filed	Number Extra	Rate		
Total Claims	20 - 20 =	- 0 -	X \$18.00	\$	
Independent Claims	3 - 3 =	- 0 -	X \$80.00	\$	
Multiple dependent claim(s) (if applicable)			+ \$270.00	\$	
TOTAL OF ABOVE CALCULATIONS =				\$ 860.00	
Reduction by 1/2 for Small Entity status.				\$	
SUBTOTAL =				\$ 860.00	
Processing fee of \$130.00 for furnishing the English translation later than ____ 20 ____ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$ 860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)) The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property +				See cover sheet attached to assign \$ to be charged to Deposit Acct	
TOTAL FEES ENCLOSED =				\$ 860.00	
				Amount to be: refunded	\$
				charged	\$

☐ Applicant claims Small Entity status.☒ A check in the amount of \$860.00 to cover the above fees is enclosed.☐ Please charge my Deposit Account No. 03-2468 in the amount of \$_____ to cover the above fees. A duplicate
copy of this sheet is enclosed.☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment, to Deposit Account No. 03-2468. A duplicate copy of this sheet is enclosed.**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or
(b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

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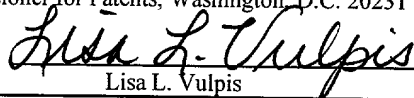
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Signature

Edward R. Freedman

Reg. No. 26,048

Express Mail No. EL 871 447 544 US**Date of Deposit September 12, 2001**I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37
CFR 1.10, on the date indicated above, and is addressed to the Ass't. Commissioner for Patents, Washington, D.C. 20231


Lisa L. Vulpis

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: MICHAEL BENJE-1 (PCT)
PCT No.: PCT/EP 99/07649 FILED: OCTOBER 12, 1999
TITLE: METHOD OF PRODUCING ETHYLENE (DI) CHLORIDE (EDC)

PRELIMINARY AMENDMENT

BOX PCT

Ass't. Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

Preliminary to Examination, please amend the above-identified application as follows:

IN THE SPECIFICATION

Page 1, after the title, please insert:

---CROSS REFERENCE TO RELATED APPLICATIONS

Applicant claims priority under 35 U.S.C. §119 of German Application No. 199 10 964.8 filed March 12, 1999. Applicant also claims priority under 35 U.S.C. §120 of PCT/EP99/07649 filed October 12, 1999. The international application under PCT article 21(2) was not published in English.--

Page 1, line 5 from below, to page 2, line 6, please amend this paragraph as follows:

A system of the first type is described, for example in DE 19 05 517, DE 25 40 257, and DE 40 39 960 A1. In the case of said system, the reaction medium is circulated by pumping via an external circulation and first aspirates the gaseous chlorine by means of a liquid-jet gas compressor. Gaseous ethylene is subsequently fed in via a perforated gas distributor. The mixed stream so produced then flows through a packing of fillers or a static mixer, where the relatively large ethylene bubbles produced by the gas distributor are dispersed, so that the ethylene dissolves at an adequate rate and reacts with the already dissolved chlorine.

A marked-up copy of the specification is shown as Exhibit A.

IN THE CLAIMS

Please cancel claims 1-20 and replace with new claims 21-40 as follows:

--21. A method of producing 1,2-dichloroethane or ethylene (di)chloride (EDC) using a circulating reaction medium and a catalyst, whereby ethylene and chlorine are supplied to the reaction medium, characterized in that the ethylene or chlorine gas are introduced into the reaction medium by means of

microporous gas diffuser elements in order to produce gas bubbles with a diameter of 0.3 to 3 mm.

22. A method of producing 1,2-dichloroethane or ethylene (di)chloride (EDC) using a circulating reaction medium and a catalyst, whereby ethylene and chlorine are supplied the reaction medium, characterized in that the chlorine is dissolved in a cooled part stream of the reaction medium and subsequently supplied to the main stream of the reaction medium.

23. A method of producing 1,2-dichloroethane or ethylene (di)chloride (EDC) using a circulating reaction medium and a catalyst, whereby ethylene and chlorine are supplied to the reaction medium, characterized in that viewed in the direction of circulation of the reaction medium, ethylene is introduced into the circulating reaction medium at a point upstream and, after passing through a mixing and dissolving zone, chlorine is supplied to the stream of reaction medium farther downstream, whereby the ethylene (di)chloride liberated with the help of the reaction of chlorine and ethylene and evaporated by the reaction heat is discharged from the reactor vessel in the gaseous state, whereas the residual amount remaining in the evaporator vessel is recycled into the reaction zone.

24. The method according to claim 21, characterized in that a medium predominantly containing 1,2-dichloroethane is used as the reaction medium.

25. The method according to claim 21, characterized in that a temperature of about 75°C to 200°C and a pressure of about 1 to 15 bar are adjusted in the mixing and reaction zone, and that the flow-through velocity is controlled in such a way that the dwelling time of the reaction mixture in the mixing and reaction zone amounts to about 1 to 30 seconds.

26. The method according to claim 21, characterized in that the EDC formed first remains in the liquid phase or evaporates within the zone of the surface of the evaporator vessel, whereby the evaporation cold is compensated by the reaction heat.

27. The method according to claim 21, characterized in that the chlorine is separately dissolved in the liquid and supplied to the reaction medium.

28. A device for carrying out the method according to claim 21, characterized by an evaporator vessel (2), a down pipe (4) and a riser (6), whereby in the direction of flow, provision is made first for an ethylene feed, subsequently for a dissolving zone, and thereafter for distributor pipes for introducing the

dissolved in a bypass stream (16) of the reaction medium into the main stream of the reaction medium.

29. The device according to claim 28, characterized in that provision is made in the flow path of the reaction medium for a circulation device for producing a forced circulation, and for a throttle valve (22) or the like for the control.

30. The device according to claim 28, characterized in that provision is made for a bypass line (16) for the reaction medium, said bypass comprising a pump (17), a heat exchanger (18) serving for cooling said part stream, a liquid-jet compressor (19) downstream for aspirating and introducing gaseous or liquid chlorine into the bypass stream, and/or a static mixer, as well as a feed into a ring line (26) with distributor tubes (14) for introducing the bypass stream into the main stream.

31. The device according to claim 28, characterized in that for measuring the flow-through in the main stream, provision is made for an ultrasound measuring device as well as for a control for actuating a flow-through control valve (22) or the like.

32. The device according to claim 28, characterized in that at least two risers (6, 6a) with the installations as defined by the invention are associated with one down pipe (4).

33. The device according to claim 28, characterized by a multitude of evaporator vessels (2) comprising one or several down pipes and risers (4, 6), whereby one or more reaction zones (12) are arranged there in the one or more circulation lines.

34. The device according to claim 28, characterized in that each unit comprising an evaporator vessel (2), a down pipe (4) and a riser (6) with installation, is realized in the form of a module with devices for coupling it with at least one or more adjacent modules.

35. The device according to claim 28, characterized in that provision is made in the bypass for a mixer with a heat exchanger as one unit in terms of device.

36. The device according to claim 28, characterized in that provision is made in the main stream for microporous gassing elements (10) for finely distributing the ethylene to be introduced.

37. The device according to claim 28, characterized in that provision is made in the reaction zone (12) for flow-rectifying devices such as baffle plates (13) throttling valves or the like.

38. The device according to claim 28, characterized in that a flow rectifier (9) is arranged upstream of the gassing elements (10) for producing a uniform velocity profile as well as for suppressing radial velocity components in the main stream.

39. The device according to claim 28, characterized in that a nozzle is arranged in the loop reactor for introducing the concentrated chlorine solution in the circulating main stream.

40. The device according to claim 28, characterized in that for introducing small amounts of preheated nitrogen, provision is made on a distributor ring (28) in the riser (6b) of the loop reactor for candles (29), the latter being made of a rough, porous material preferably consisting of ceramics or sintered metal (FIG. 6).--


REMARKS

By this Preliminary Amendment, a cross-reference to related applications has been inserted in page 1. A typographical error in the number of a reference has been corrected on page 1. Original claims 1-20 have been replaced with new claims 21-40 so that the multiple dependency of certain of the dependent claims has been removed to avoid the surcharge associated therewith. No

new matter has been introduced. Entry of this amendment is respectfully requested.

Respectfully submitted,
MICHAEL BENJE

By:


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Enclosure: Exhibit A

EXPRESS MAIL NO. **EL 871 447 544 US**

Date of Deposit: September 12, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, on the date indicated above, and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.


Lisa L. Vulpis

EXHIBIT A

A MARKED-UP VERSION WITH MARKINGS TO SHOW
CHANGES MADE TO THE SPECIFICATION

Page 1, please amend paragraph 3 through to page 2 as follows:

A system of the first type is described, for example in DE 19 05 517, DE 25 [42 057] 40 257, and DE 40 39 960 A1. In the case of said system, the reaction medium is circulated by pumping via an external circulation and first aspirates the gaseous chlorine by means of a liquid-jet gas compressor. Gaseous ethylene is subsequently fed in via a perforated gas distributor. The mixed stream so produced then flows through a packing of fillers or a static mixer, where the relatively large ethylene bubbles produced by the gas distributor are dispersed, so that the ethylene dissolves at an adequate rate and reacts with the already dissolved chlorine.

3/pr.1s

METHOD OF PRODUCING ETHYLENE (DI)CHLORIDE (EDC)

The invention relates to a method for producing 1,2-dichloroethane or ethylene (di)chloride (EDC), using a circulating reaction medium and a catalyst, whereby ethylene and chlorine are supplied to the reaction medium.

The production of 1,2-dichloroethane on a large technical scale is carried out by introducing the gaseous reaction partners chlorine and ethylene into a circulating reaction medium (1,2-dichloroethane in most cases) that contains a suitable catalyst (e.g. iron(III)chloride) in the dissolved form. In designing the reaction systems employed for said purpose, a distinction is made between concepts in connection with which the reaction medium is circulated by pumping, and those in conjunction with which the reaction medium is circulated by both the mammoth pumping effect of the gaseous reaction partners that are metered in, and the natural circulation that is produced by the reaction heat.

A system of the first type is described, for example in DE 19 05 517, DE 25 42 057, and DE 40 39 960 A1. In the case of said system, the reaction medium is circulated by pumping via an external circulation and first aspirates the gaseous chlorine by means of a liquid-jet gas compressor. Gaseous

ethylene is subsequently fed in via a perforated gas distributor. The mixed stream so produced then flows through a packing of fillers or a static mixer, where the relatively large ethylene bubbles produced by the gas distributor are dispersed, so that the ethylene dissolves at an adequate rate and reacts with the already dissolved chlorine.

The use of a static mixer is described in EP 0 471 987 B1. Thus the packing of fillers or the static mixer represent the actual reaction line.

In addition to aspiration and fine distribution or dissolution of the reaction partners, the stream circulated by pumping performs a further function: dissipation of the reaction heat. The reaction heat amounts to about 2,200 kJ/kg EDC, i.e. the amount of heat collected in the production of 1 ton of EDC suffices for generating approximately 1 ton of steam. The circulated amount therefore has to be large enough to prevent boiling from occurring along the reaction line.

In the system described in the patent documents cited above, the reactor content does not boil, but the hot circulating stream is rather divided in two partial streams. The larger part stream serves for indirectly heating columns, whereas the smaller part stream is partially relieved. The gaseous stream

produced by the relief evaporation corresponds with the quantity produced and can be directly fed into a column for a purification treatment.

A special drawback of the known procedure consists in the fact that the stream circulated by pumping is very large, so that large pumps with high capacities are required, which conditions high investment and operating costs.

In the other system operating with natural circulation, the required circulation of the liquid is produced by the mammoth pumping effect of the gaseous reaction partners or by natural convection due to the liberated reaction heat. The circulation of the liquid can take place in this connection via an external pipeline or also in the reactor vessel itself.

Said method is described, for example in DE-OS 24 27 045. In said process, the reaction medium circulates via an external pipeline and the reaction partners are admitted into the circulating stream via gas distributors. The reaction mixture subsequently flows through a packing that represents the reaction line. The circulating amount can be controlled by means of a fitting. With the present concept, the reactor content is boiling. It is therefore necessary to assure through an adequate geodetic level and corresponding positioning of the

reaction line and also through adjustment of a sufficiently large circulating stream that no boiling will occur along the reaction line. A drawback of said system is that the chlorine is not aspirated and compressed by a liquid-jet gas compressor, but has to be already available at a certain minimum pressure, which is often not the case, so that pre-compression of the chlorine may be required.

Both systems have in common that a local excess of chlorine may be present at the start of the reaction line, which favors the formation of higher-chlorinated by-products. This has its cause in the fact that chlorine is by multiple times more soluble in 1,2-dichloroethane than ethylene. This has the following consequences in both of the systems described above:

With the first system (forced circulation with pumps), the chlorine is immediately very finely distributed by the high shearing forces acting in the liquid-jet gas compressor, and is received already highly dissolved at the point where the ethylene is added. This means that an excess of chlorine is already on hand when the ethylene starts to dissolve.

With the second system (natural circulation), the added chlorine dissolves along the reaction line at a higher rate than the ethylene. An excess amount of chlorine is present at

least at the start of the reaction line in that case as well.

The problem of the present invention is to provide a solution by which the catalytic chlorination of ethylene is made possible in a manner that is particularly gentle for the product, whereby the reaction heat generated in the course of the reaction is employed in a useful manner and the undesirable formation of highly chlorinated products such as tri-, tetra- and pentachloroethane in the reactor is largely avoided. Said benefits are combined with a plant concept that permits a modular type of expansion of the system at favorable cost.

In a process of the type specified above, said problem is solved according to the invention in that the ethylene or the chlorine gas is introduced into the reaction medium by means of microporous gas diffuser elements employed for producing gas bubbles having a diameter of from 0.3 to 3 mm.

Said special manner of introducing the gases into the reaction medium achieves an adequately fine distribution and thus an optimal production result. Introducing said gas bubbles with the size as defined by the invention is possible in a comparatively simple manner. Special devices for admitting the gas bubbles are specified farther below.

A contribution to the solution of the problem that is based on the same starting point consists in that the chlorine is dissolved in a cooled part stream of the reaction medium and then supplied to the main stream of the reaction medium. The problem as defined by the invention can be solved by said measure as well, notably the catalytic chlorination of ethylene in a manner that is especially gentle for the product.

Finally, the invention makes provision that viewed in the direction of circulation of the reaction medium, ethylene is introduced into the circulating medium at a point upstream, and, after passing through a mixing and dissolving zone, chlorine is supplied to the reaction medium at a point farther downstream, whereby the ethylene (di)chloride that is liberated in the reaction of the chlorine and ethylene and evaporated by the reaction heat, is discharged from the reaction vessel in the gaseous state, whereas the residual amount remaining in the evaporation vessel is recycled into the reaction zone.

The method as defined by the invention permits achieving optimal results because the partners participating in the process each have adequate time to react. For example, the ethylene can pass through the free dissolution line located between the ethylene distributor, on the one hand, and the start of the chlorine distributor on the other, and is capable

of dissolving completely owing to the small starting size of the bubbles produced by the microporous gas diffuser elements, so that the subsequent reaction takes place in solution.

Apart from providing for only one point at which the ethylene is added, it is, of course, possible also to make provision for several of such points of addition. In any case, the formed EDC first remains in the liquid phase and evaporates only within the zone of the surface of the evaporator vessel, whereby the evaporation cold is compensated by the reaction heat.

The reaction partners ethylene and chlorine may be diluted with inert gases.

The use of iron(III)-chloride as the catalyst, for example, can be recommended. For avoiding the formation of by-products, it is possible also to use, for example oxygen as an inhibitor.

Further developments of the procedure as defined by the invention are specified in the dependent claims, whereby it is useful to employ as the reaction medium, for example a medium predominantly containing 1,2-dichloroethane. As process parameters, it is recommended to adjust a temperature of about

75° to 200°C and a pressure of about 1 to 15 bar in the mixing and reaction zone, and to control the rate of flow-through in such a way that the dwelling time of the reaction mixture in the mixing and reaction zone amounts to from 1 to 30 seconds.

Finally, provision is made, furthermore, that the chlorine is added to the main stream of the reaction medium at the end of the mixing and reaction zone, said chlorine having first been dissolved in an undercooled part stream of the reaction medium. Dissolving the chlorine in an undercooled part stream offers the advantage that a particularly large amount of chlorine is dissolved in that case, and is possible to make do with a comparatively small amount of liquid or with smaller pumps. The fact that the solubility of the chlorine is rising as the temperature is dropping is advantageously exploited in this manner.

Alternatively, it is possible also to make provision that the chlorine is dissolved in a separate liquid circulation, for example in 1,2-dichloroethane, and then added to the reaction medium.

Furthermore, for solving the problem, the invention make provision for a device for carrying out the method as defined by the invention. Said device is characterized by an evaporator

vessel, a down pipe and a rising pipe, whereby provision is made in the riser in the direction of flow first for an ethylene feed, subsequently for a dissolving zone, and following the latter for distributor tubes for admitting chlorine into the main stream of the reaction medium, such chlorine having first been dissolved in a bypass stream of the reaction medium.

Further developments of the invention are specified in the dependent claims relating to the device as defined by the invention. For example, provision can be made in the flow path of the reaction medium for a circulation device for producing a forced circulation, and for controlling purposes for a throttling valve or the like. It has to be noted at this point that the natural circulation is a joint object of the present invention, whereby provision can be made for similar control elements in the flow path of such natural circulation.

As a further development of the invention, provision can be made for a bypass line for the reaction medium, such bypass comprising a pump, a heat exchanger for cooling said bypass part stream, a liquid-jet compressor downstream for aspirating and introducing gaseous or liquid chlorine into the bypass stream, and/or for a static mixer, as well as for a feed

leading into a ring conduit with distributor tubes for feeding the bypass stream into the main stream.

So that the flow-through can be controlled in a very precise manner, the invention, furthermore, provides for a further development in that provision is made for an ultrasound measuring device for measuring the flow-through in the main stream, as well as for a control means for actuating a flow-through control valve or the like.

At least two risers comprising the installations as defined by the invention may be associated with one down pipe. Furthermore, a multitude of evaporator vessels comprising one or more down pipes and risers can be arranged according to the invention in a suitable manner, whereby one or more reaction zones are arranged in such a system in the one or more circulation pipelines.

Said further developments of the invention make it possible to design the device as a type of modular construction. It is advantageous for said purpose if each unit comprising an evaporator vessel, a down pipe and a riser with installations is designed in the form of a module with devices for coupling it with at least one adjacent module or a number of such modules. Another preferred embodiment is the one that comprises

an evaporator vessel with a plurality of risers and down pipes, or with a central down pipe and a plurality of risers starting from said down pipe.

Other embodiments of the invention consist in that provision is made in the bypass for a mixer with a heat exchanger as one unit in terms of device, and/or that microporous gas diffuser elements are provided in the main stream for finely distributing the ethylene to be introduced, and/or that elements such as baffle plates, throttling valves or the like are installed in the reaction zone for rectifying the flow.

A further advantageous embodiment of elements of the device as defined by the invention consists in that upstream of the gassing elements, a device for rectifying the flow is arranged in the main stream for producing a uniform velocity profile, as well as for suppressing radial velocity components.

Further features, details and advantages of the invention issue from the following description as well as from the drawing, in which:

FIG. 1 is a simplified flow diagram of the device as defined by the invention.

FIG. 2 is a partly enlarged cutout from the riser of the device as defined by the invention, comprising symbolically indicated installations.

FIGS. 3 and 4 are simplified sectional drawings according to lines III-III and, respectively, IV-IV in FIG. 2.

FIG. 5 shows a partial view of a pipe area with a driving jet nozzle, and

FIG. 6 shows a cutout of a part tube with a nitrogen feed nozzle.

The device for carrying out the method for producing EDC with the use of a circulating reaction medium is generally denoted in FIG. 1 by reference numeral 1 and substantially shown only symbolically and highly simplified.

FIG. 1 shows an evaporator vessel 2 with an indicated stream dome 3 and a down pipe 4 that merges via a transition line 5 into a rising pipe generally denoted by 6, said riser in turn feeding into the evaporator vessel 2. Following the down pipe to the right, FIG. 1 shows by a dash-dotted line that a transition line 5a and a rising pipe 6a are associated with said down pipe, whereby the evaporator vessel 2 is divided via

the dash-dotted lines 7, which indicate that the device can be realized in the form of a modular construction, i.e. provision can be made for a plurality of risers on an evaporator vessel 2 that has been extended in a modular manner. Said evaporator also may comprise more than one down pipe, if necessary, which, however, is not important in this connection.

FIG. 1 shows that the flow follows a defined direction either by natural or forced circulation, said direction being indicated in FIG. 1 by the arrows 8. After passing through the transition line 5, provision is made in the riser 6 in the direction of flow first for a flow rectifying device 9 in order to produce a uniform axial velocity profile and to suppress radial velocity components. Said flow-rectifying device 9 is followed by a series of the microporous gas diffuser elements 10, by way of which pearls of ethylene can be introduced into the circulating reaction medium via the line 11.

Thereafter, provision is made in the riser for a dissolution zone denoted by 12, which in turn is followed downstream by an installation 13 for producing a uniform flow, and for a feeding element 14 for feeding in chlorine dissolved in the reaction medium. The feed line for said reaction medium/chlorine mixture is denoted by 15.

Via a line 16, a part stream is tapped from the reaction medium as the bypass stream 16 and then supplied to a cooler 18 by a pump 17, whereby the chlorine supplied via the line 20 is admixed to said bypass stream via a liquid-jet compressor 19, whereby provision can be made in the flow path for a static mixer 21 as well.

For regulating the circulation, provision is made in the down pipe 4 for a symbolically indicated throttling valve 22. The position of said throttling valve is controlled, for example by means of an ultrasound measuring method for measuring the flow-through, said control being generally denoted by 23.

For the start-up operation, a part stream of the bypass stream 16 can be supplied via a line 24 to a distributor nozzle 25 which, in the transition zone 5 from the down pipe 4 to the riser 6, provides for the required flow, whereby the heat exchanger 18 can then be employed as a heater as well.

The arrangement and positioning of the gas diffuser element 10 as well as of the feed elements 14 for feeding the ethylene, on the one hand, and the reaction medium/chlorine mixture on the other, are shown in FIGS. 2 to 4 in slightly greater detail, with only examples being shown in said figures.

FIG. 2 in association with FIG. 4 shows that the microporous gas diffuser elements 10 are arranged in the form of a star in the interior of the riser 6 and acted upon by the line 11, whereby such an arrangement is not mandatory. The feed elements 14, on the other hand, are mounted on a ring channel 26, which is only indicated in FIG. 2 in association with FIG. 3 as well.

FIG. 5 shows the possibility for providing a nozzle 27 in the transition line, which is denoted here by 5'. The part EDC stream 15', into which the chlorine 20' was previously introduced, for example via a liquid-jet compressor 19', is introduced via said nozzle. Said part stream can be employed as a driving jet in order to support the flow in the loop reactor 1.

FIG. 6 shows the possibility for making provision for supplying small amounts of preheated nitrogen via a ring line 28, for example on the riser 6b, in order to prevent retardation of ebullition (flow surges), whereby the ring line 28 is provided with the candles 29 made of a rough porous material, as this is indicated in FIG. 6.

The described exemplified embodiment of the invention can, of course, still be modified in many different ways without vacating the basic idea of the invention. For example, the

invention is in particular not limited to the special arrangement and embodiment of the gas diffusion elements 10 shown in the present case , on the one hand, and the feeding elements 14 on the other, and is also not limited to a certain type of control system, although the control selected in the present case is particularly useful. The gas diffuser elements can be provided also in the down pipe because the dissolution of the ethylene may take place also in the down pipe, whereby the gas bubbles produced are transported downwards by the liquid stream (the velocity of the flow of the liquid produced by the circulation is greater than the velocity at which the gas bubbles rise).

Claims

1. A method of producing 1,2-dichloroethane or ethylene (di)chloride (EDC) using a circulating reaction medium and a catalyst, whereby ethylene and chlorine are supplied to the reaction medium, characterized in that the ethylene or chlorine gas are introduced into the reaction medium by means of microporous gas diffuser elements in order to produce gas bubbles with a diameter of 0.3 to 3 mm.

2. A method of producing 1,2-dichloroethane or ethylene (di)chloride (EDC) using a circulating reaction medium and a catalyst, whereby ethylene and chlorine are supplied to the reaction medium, characterized in that the chlorine is dissolved in a cooled part stream of the reaction medium and subsequently supplied to the main stream of the reaction medium.

3. A method of producing 1,2-dichloroethane or ethylene (di)chloride (EDC) using a circulating reaction medium and a catalyst, whereby ethylene and chlorine are supplied to the reaction medium, characterized in that viewed in the direction of circulation of the reaction medium, ethylene is introduced into the circulating reaction medium at a point upstream and, after passing through a mixing and dissolving zone, chlorine is

supplied to the stream of reaction medium farther downstream, whereby the ethylene (di)chloride liberated with the help of the reaction of chlorine and ethylene and evaporated by the reaction heat is discharged from the reactor vessel in the gaseous state, whereas the residual amount remaining in the evaporator vessel is recycled into the reaction zone.

4. The method according to any one of the preceding claims, characterized in that a medium predominantly containing 1,2-dichloroethane is used as the reaction medium.

5. The method according to any one of the preceding claims, characterized in that a temperature of about 75°C to 200°C and a pressure of about 1 to 15 bar are adjusted in the mixing and reaction zone, and that the flow-through velocity is controlled in such a way that the dwelling time of the reaction mixture in the mixing and reaction zone amounts to about 1 to 30 seconds.

6. The method according to any one of the preceding claims, characterized in that the EDC formed first remains in the liquid phase or evaporates within the zone of the surface of the evaporator vessel, whereby the evaporation cold is compensated by the reaction heat.

7. The method according to any one of the preceding claims,

characterized in that the chlorine is separately dissolved in the liquid and supplied to the reaction medium.

8. A device for carrying out the method according to any one of the preceding claims, characterized by an evaporator vessel (2), a down pipe (4) and a riser (6), whereby in the direction of flow, provision is made first for an ethylene feed, subsequently for a dissolving zone, and thereafter for distributor pipes for introducing the chlorine dissolved in a bypass stream (16) of the reaction medium into the main stream of the reaction medium.

9. The device according to claim 8, characterized in that provision is made in the flow path of the reaction medium for a circulation device for producing a forced circulation, and for a throttle valve (22) or the like for the control.

10. The device according to claim 8 or 9, characterized in that provision is made for a bypass line (16) for the reaction medium, said bypass comprising a pump (17), a heat exchanger (18) serving for cooling said part stream, a liquid-jet compressor (19) downstream for aspirating and introducing gaseous or liquid chlorine into the bypass stream, and/or a static mixer, as well as a feed into a ring line (26) with distributor tubes (14) for introducing the bypass stream into

the main stream.

11. The device according to claim 8 or any one of the succeeding claims, characterized in that for measuring the flow-through in the main stream, provision is made for an ultrasound measuring device as well as for a control for actuating a flow-through control valve (22) or the like.

12. The device according to claim 8 or any one of the succeeding claims, characterized in that at least two risers (6, 6a) with the installations as defined by the invention are associated with one down pipe (4).

13. The device according to claim 8 or any one of the succeeding claims, characterized by a multitude of evaporator vessels (2) comprising one or several down pipes and risers (4, 6), whereby one or more reaction zones (12) are arranged there in the one or more circulation lines.

14. The device according to claim 8 or any one of the succeeding claims, characterized in that each unit comprising an evaporator vessel (2), a down pipe (4) and a riser (6) with installation, is realized in the form of a module with devices for coupling it with at least one or more adjacent modules.

15. The device according to claim 8 or any one of the subsequent claims, characterized in that provision is made in the bypass for a mixer with a heat exchanger as one unit in terms of device.

16. The device according to claim 8 or any one of the succeeding claims, characterized in that provision is made in the main stream for microporous gassing elements (10) for finely distributing the ethylene to be introduced.

17. The device according to claim 8 or any one of the succeeding claims, characterized in that provision is made in the reaction zone (12) for flow-rectifying devices such as baffle plates (13) throttling valves or the like.

18. The device according to claim 8 or any one of the succeeding claims, characterized in that a flow rectifier (9) is arranged upstream of the gassing elements (10) for producing a uniform velocity profile as well as for suppressing radial velocity components in the main stream.

19. The device according to claim 8 or any one of the succeeding claims, characterized in that a nozzle is arranged in the loop reactor for introducing the concentrated chlorine solution in the circulating main stream.

20. The device according to claim 8 or any one of the succeeding claims, characterized in that for introducing small amounts of preheated nitrogen, provision is made on a distributor ring (28) in the riser (6b) of the loop reactor for candles (29), the latter being made of a rough, porous material preferably consisting of ceramics or sintered metal (FIG. 6).

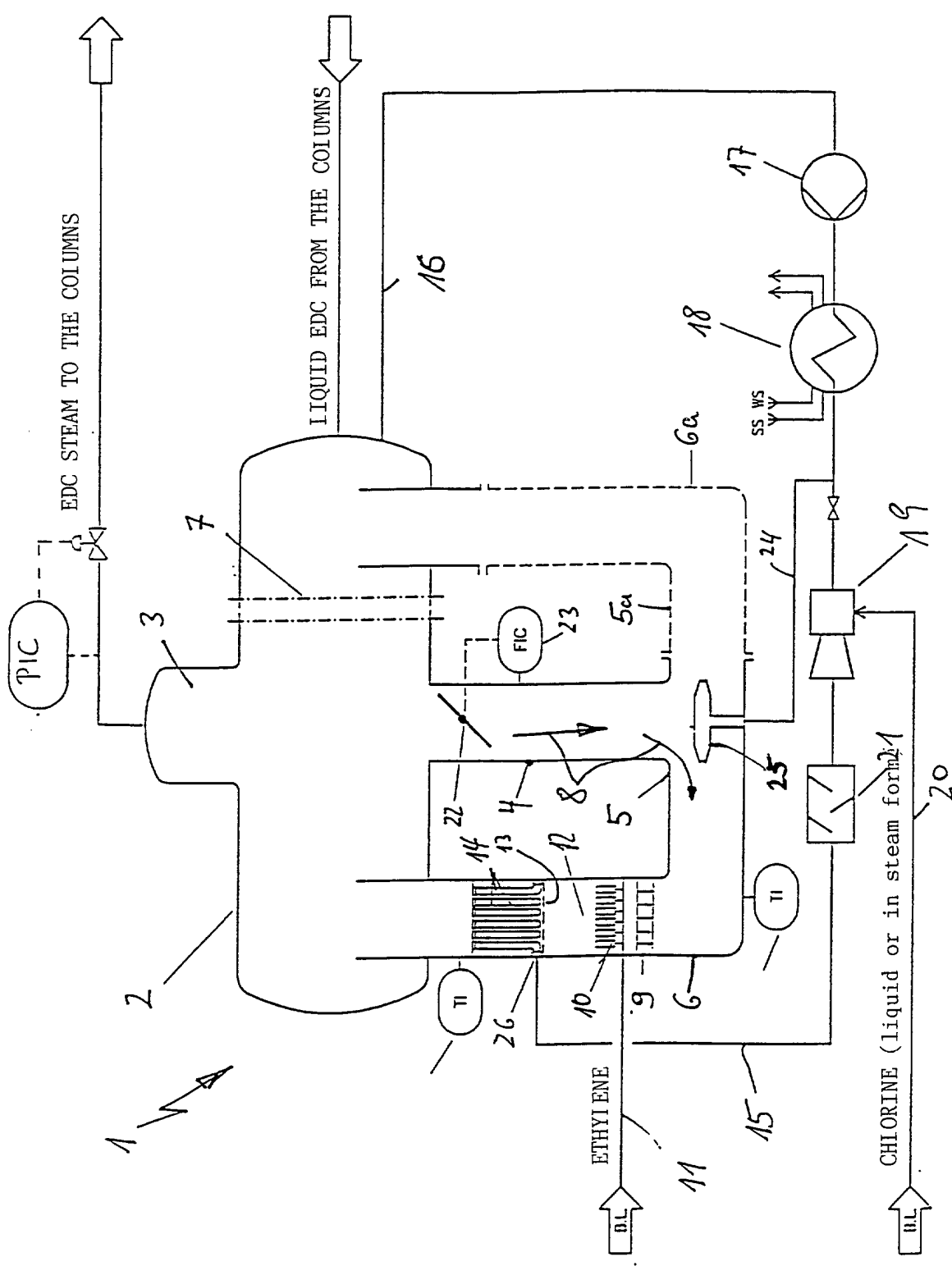
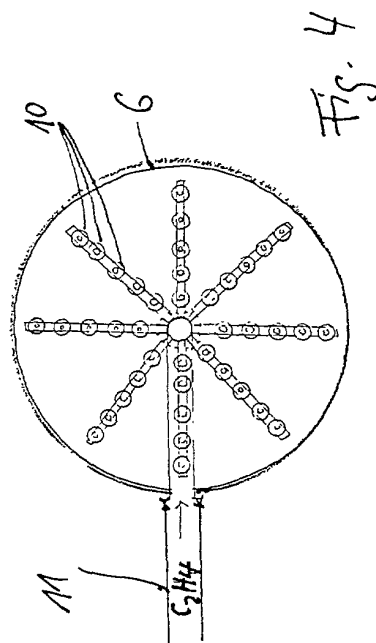
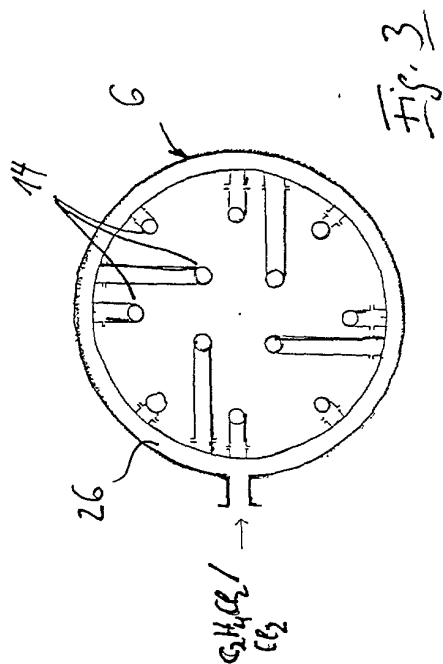
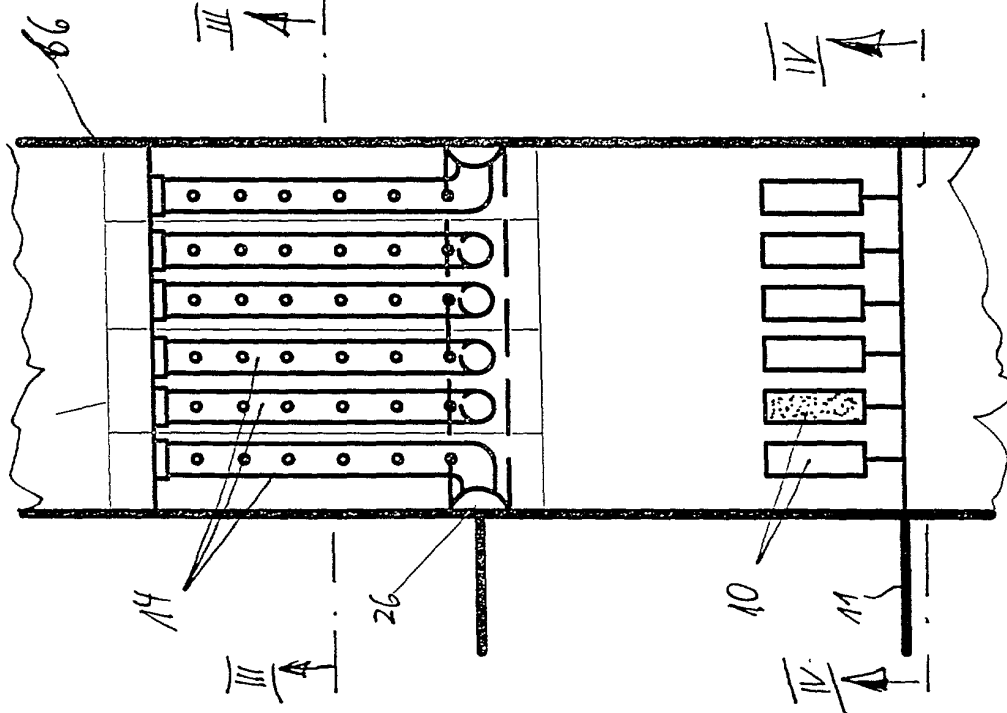


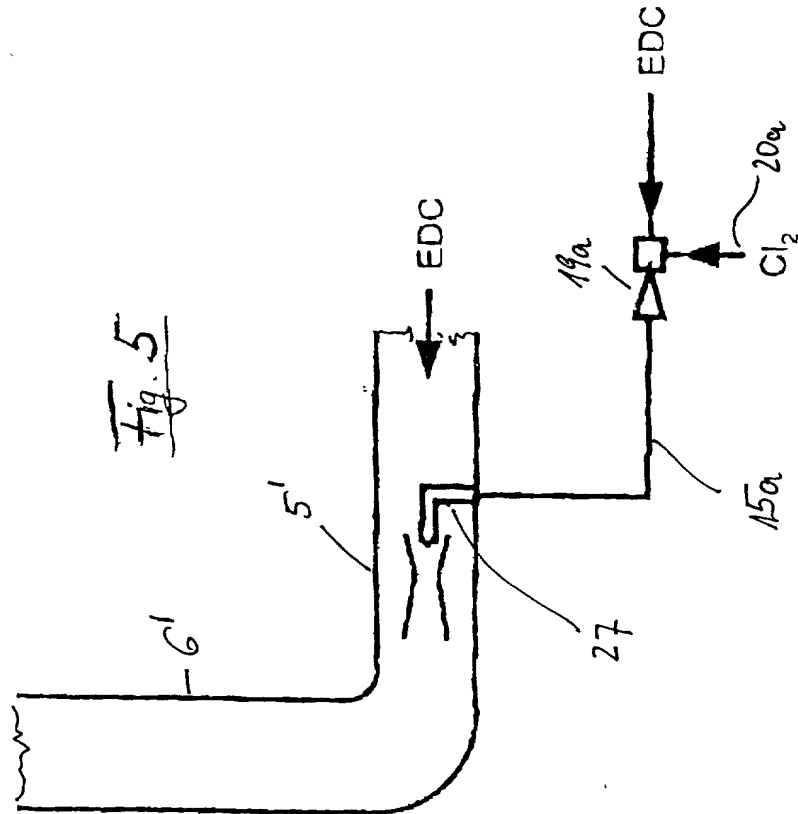
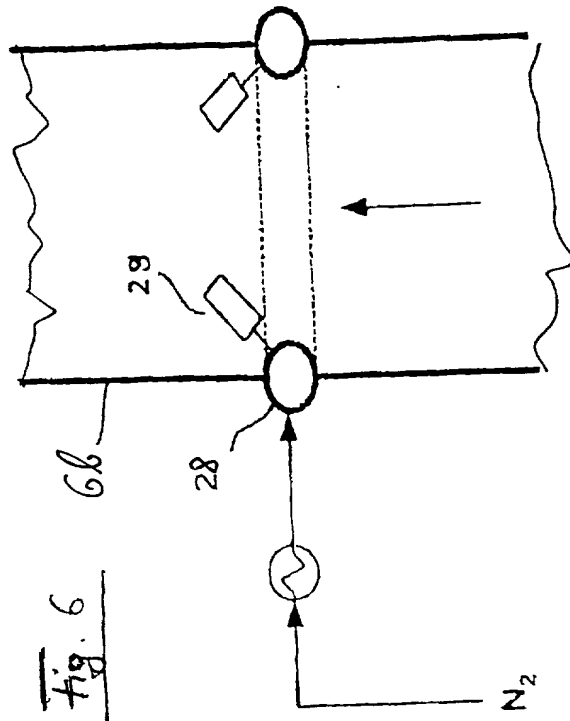
Fig. 1

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As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD OF PRODUCING ETHYLENE (DI) CHLORIDE (EDC)

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Serial No. _____

on _____,

and was amended

on _____ (if applicable).

☒ was filed as PCT international application

Number PCT/EP99/07649

on 12 OCTOBER 1999,

and was amended under PCT Article 19

on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. 119
GERMANY	199 10 964.8	12 MARCH 1999	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
(Includes Reference to PCT International Applications)

ATTORNEY'S DOCKET NUMBER
BENJE-1 PCT

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclose in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR
BENEFIT UNDER 35 U.S.C. 120:

U.S. APPLICATIONS			STATUS (Check One)		
U.S. APPLICATION NUMBER	U S FILING DATE		PATENTED	PENDING	ABANDONED
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)			

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration numbers):

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201

DATE

Michael Benje
16.07.01